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(54) Title: **HOLLOW BEADS OF POLYETHYLENE**

(57) Abstract: The present invention discloses a method for preparing hollow beads of polyethylene of controlled morphology and size.

HOLLOW BEADS OF POLYETHYLENE.

5

This invention is related to the field of hollow beads of polyethylene and their method of preparation. It also relates to the catalyst components used in their preparation.

10

Iron-based catalyst systems have been described in literature for the polymerization or oligomerisation of olefins.

For example by Britovsek et al. (G.J.P. Britovsek, V.C. Gibson, B.S. Kimberlay, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White and D.J. Williams, in Chem. Comm. , 1998, 849.) describe novel olefin polymerization catalysts based on iron and cobalt that are active for the polymerization of olefins, particularly ethylene.

Small, Brookhart and Bennett (B.L. Small, M. Brookhart and A.M.A. Bennett, in J. Am. Chem. Soc., 1998, 4049.) describe an iron and cobalt catalysts that are very active for the polymerisation of ethylene.

Small and Brookhart (B.L. Small and M. Brookhart, in Macromolecules, 1999, 2120.) disclose a new generation of iron catalysts for the polymerization of propylene.

Some other research groups such as for example Roscoe et al. (S.B. Roscoe, J.M. Fréchet, J.F. Walzer and A.J. Dias, in Science, 1998, vol. 280, 270.) have been able to produce polyolefin spheres from metallocenes supported on non-interacting polystyrene support.

Liu and Jin (C. Liu and G. Jin, in New J. Chem. 2002, 1485.) disclose a method for immobilizing an iron-based catalyst on polystyrene chains.

None of these prior art documents have addressed the problem of preparing hollow beads of polyethylene of controlled morphology and size.

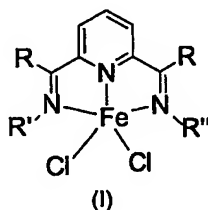
The present invention discloses a method for preparing hollow beads of polyethylene of controlled morphology and size.

The present invention also discloses a supported iron-based catalyst component very active in the preparation hollow beads of polyethylene.

10 The present invention further discloses a method for preparing the supported iron-based catalyst component.

Accordingly, the present invention discloses a method for preparing hollow beads of polyethylene of controlled morphology and size that comprises the steps of:

- 15 a) providing a supported catalyst component wherein the support is a porous functionalised bead of polystyrene and wherein the catalyst component is impregnated on the support and is an iron based complex of general formula



20

wherein R is the same and is an alkyl having from 1 to 20 carbon atoms and wherein R' and R'' are the same or different and are a substituted or unsubstituted alkyl having from 1 to 20 carbon atoms, or a unsubstituted or substituted aryl having substituents from 1 to 20 carbon atoms;

25

- b) activating the support with a suitable activating agent;
c) feeding the ethylene monomer;
d) maintaining under polymerization conditions;

e) retrieving hollow beads of polyethylene of controlled morphology and size.

R are the same and are preferably an alkyl having from 1 to 4 carbon atoms, more preferably, it is methyl.

5

R' and R" are the same or different and are selected from a substituted or unsubstituted alkyl having from 1 to 6 carbon atoms or are a unsubstituted or substituted aryl having substituents from 1 to 6 carbon atoms. Preferably, R' and R" are the same and are phenyls. The substituents on the phenyls, if present, can
10 have either an inductive attracting, donating effect or a steric effect.

The substituents that have an inductive attracting or donating effect can be selected from hydrogen or an alkoxy, or NO₂, or CN, or CO₂R or an alkyl having from 1 to 20 carbon atoms, or a halogen or CX₃ wherein X is a halogen, preferably
15 fluor, or a fused ring between positions 3 and 4, or between positions 4 and 5 or between positions 5 and 6.

The steric environment of the iron-based complex is determined by the substituents at positions 2 and 6 and optionally at positions 3, 4 and 5 on the phenyls.

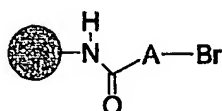
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For the steric effect, the preferred substituents on the phenyls, if present, can be selected from tert-butyl, isopropyl or methyl. The most preferred substituents are isopropyl in positions 2 and 6 or methyl in positions 2, 4 and 6.

25 The present invention discloses a supported catalyst component, very active in the preparation of hollow beads of polyethylene of controlled morphology and size, that comprises a support prepared from a porous bead of functionalised polystyrene and an iron-based complex that is impregnated on the support.

30 The present invention also discloses a method for preparing the supported catalyst component that comprises the steps of:

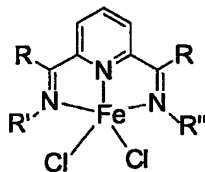
a) providing a porous functionalised bead of polystyrene of formula II;



5

(II)

b) dissolving the iron-based complex of formula I in dichloromethane;



(I)

- 10 c) saturating the bead of step a) with the solution of step b);
 d) evaporating the solvent;
 e) retrieving dry beads of the supported catalyst component.

15 All reactions are carried out in inert atmosphere at room temperature of about 20 °C and under atmospheric pressure.

20 The starting porous functionalised beads of polystyrene have a size of from 250 to 500 microns and they are prepared from cross linked polystyrene wherein the degree of cross linking is ranging from 0.5 to 5 %. A proper level of cross linking must be selected: it must be sufficiently high to insure shape constraint but

sufficiently low to allow absorption of the active ingredients. A degree of cross linking of from 1 to 2 % is preferred.

A catalyst system is then prepared by activating the supported catalyst component
5 with a suitable activating agent.

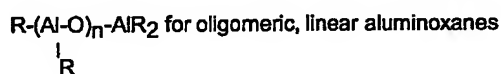
The activating agent can be selected from aluminoxanes or aluminium alkyls.

The aluminium alkyls are of the formula AlR_x and can be used wherein each R is
10 the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminiumalkyl are dialkylaluminum chloride, the most preferred being diethylaluminum chloride (Et_2AlCl).

15 Aluminoxane is used to activate the catalyst component during the polymerisation procedure, and any aluminoxane known in the art is suitable.

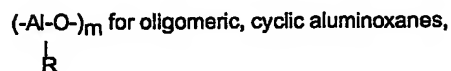
The preferred aluminoxanes comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by the formula :

20



and

25



wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8
30 alkyl group and preferably methyl.
Methylaluminoxane (MAO) is preferably used.

The hollow beads of polyethylene have a diameter of from 0.5 to 2 mm as can be seen on Figure 1 representing the starting beads of polystyrene and the final beads of polyethylene. The beads have a very narrow size distribution.

- 5 The catalytic activity is governed by the nature of the substituents R' and R'' on the phenyl groups.

List of Figures.

- 10 Figure 1 represents the starting polystyrene beads and the final polyethylene hollow beads.

Figure 2 represents a hollow bead of polyethylene. Figure 2a is an external view and Figure 2b is an internal view of the bead.

15

Examples.

The starting materials and reagents, purchased from commercial suppliers, were used after standard purifications. The solvents were dried and distilled before use

- 20 as follows:

- over sodium and benzophenone for toluene and tetrahydrofuran (THF),
- over sodium for methanol and
- over phosphorus pentoxide for dichloromethane (DCM).

Manipulations were all performed on a vacuum line under argon, using standard

- 25 Schlenk tube techniques or in Jacomex glove box.

The rotating shaker is a Labquake shaker.

NMR spectra were recorded on a Bruker DPX 200 at 200 MHz (for ^1H) and 50MHz (for ^{13}C).

Infrared ATR (silicium) spectra were recorded in the range 4000-400 cm^{-1} on a IR

- 30 Centaurus microscope.

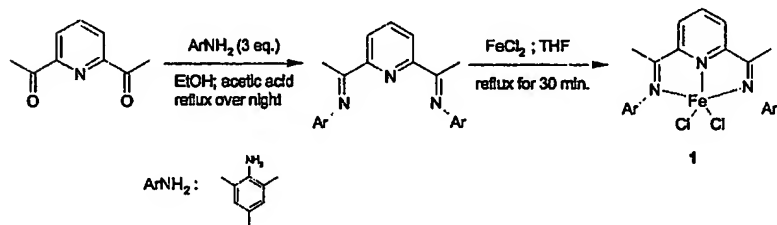
High resolution mass spectra were obtained on a Varian MAT 311 (electronic ionisation mode) at CRMPO, University of Rennes.

Elemental analysis were performed by the CNRS laboratory, Vernaison (France).

Synthesis of the catalyst

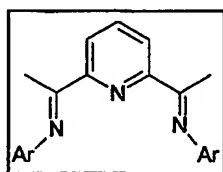
The synthesis of bisimines from 2,6-diacetylpyridine was performed as described for example in Britovsek et al. (G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, in J. Am. Chem. Soc., 1999, 8728.). To form the iron complex, the procedure described in Small and Brookhart (L. Small and M. Brookhart, In Macromolecules, 1999, 2120.) was applied, *i.e.* iron (II) chloride was added to the bisimines in THF. The reaction was allowed to stir at reflux for 30 minutes. The reaction mixture was cooled at room temperature. The precipitate of iron complex appeared and the mixture was filtrated. The precipitate was dried under vacuum.

15



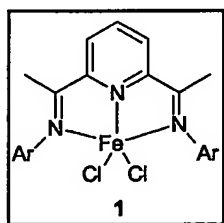
To a refluxed homogenous solution of 163 mg (1 mmol) of 2,6-diacetylpyridine in 3 mL of absolute ethanol under argon atmosphere were added 406 mg (3 mmol) of 2,4,6-trimethylaniline. After the addition of a few drops of glacial acetic acid, the solution was refluxed for 20 hours at 90 °C.

Upon cooling to room temperature, the product crystallized from ethanol. After filtration the yellow solid was washed with cold ethanol and dried under reduced pressure to give 0.164 g (42%) of the bisimine.



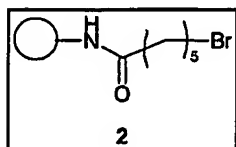
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- 45.77 mg (0.23 mmol) of iron (II) chloride tetrahydrate were dried under reduced pressure at 120°C during 5 hours. The iron (II) chloride was added to the bisimines in THF. The reaction was allowed to stir at reflux for 30 minutes. The reaction mixture was cooled at room temperature. The precipitate of iron complex appeared and the mixture was filtrated and dried under reduced pressure to give 0.104 g (87%) of the blue complex 1.



- Under argon, to 177 mg (0.2 mmol) of polystyrene AM-NH₂ beads purchased from Rapp polymere (1,13 mmol/g, 250-315 µm) in 3.6 mL of dichloromethane (DCM) were slowly added 0.44 mL (0.3 mmol) of triethylamine followed by a careful addition of 0.36 mL (2.4 mmol) of 6-bromohexanoyl chloride. The reaction mixture was stirred for 2h at room temperature on a rotating shaker before being drained.
- The beads were then washed twice for 30 minutes with dimethylformamide, twice for 10 minutes with DCM, twice for 10 minutes with methanol, twice for 30 minutes

with dimethylformamide, twice for 10 minutes with DCM, twice for 30 minutes with methanol and then dried under reduced pressure to give 0.2 mmol of the white beads 2. A Kaiser test was performed to verify sure the reaction was complete.



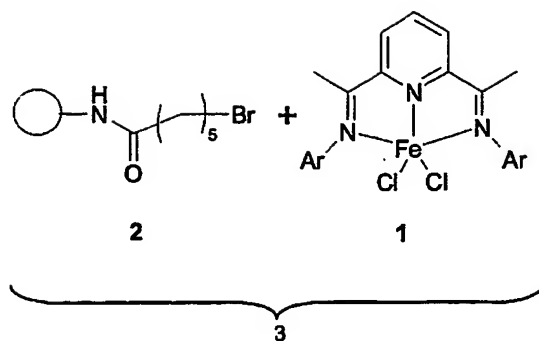
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Impregation of porous beads.

The following reaction was entirely performed in a glove box. A 8.9×10^{-3} M solution of iron complex (1) in DCM was prepared by dissolving 0.233 mg (0.0448 mmol) of complex (1) in 5 mL of DCM. This solution was added to the beads (2). The mixture was stirred at room temperature for 2 hours on a rotating shaker. They were then drained, washed quickly with 2 mL of DCM and then dried under reduced pressure. The same solution of iron complex (1) was prepared again and added to the beads a second time. The mixture was stirred at room temperature for 2 hours on a rotato. They were drained, washed quickly with 2 mL of DCM and then dried under reduced pressure to give the blue beads (3). The amount of iron was measured as:

Fe (ICP AES) : 630 ppm (wt).

20 Total loading of beads (3): 1.128×10^{-2} mmol Fe / g of beads.



5

Polymerisation of ethylene.

10

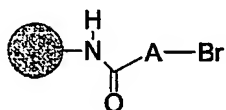
Under argon, 55 mL of toluene (55 ml), followed by 3.2 mL of MAO (30%wt in toluene) were added in a 200 mL stainless steel reactor. The reactor was flushed with argon for 5 minutes. 8.4 mg of the dried beads (3) (9.47×10^{-8} mol Fe) were quickly injected, with the help of 2 mL of toluene added 2 minutes before, in the reactor. The reactor was again flushed with argon for 5 minutes. The temperature was raised to 50°C, the reactor was put under 20 bar of ethylene and the reaction mixture was stirred for 3 hours. When the reaction mixture was back to room temperature and under argon, the solution was taken off, the beads were washed with ethanol and dried under reduced pressure to give 0.727 g porous spheric polyethylene particles. The activity was measured as 7.67 Tons of polyethylene produced per mole of iron.

20

CLAIMS.

- 5 1. A method for preparing a supported catalyst component for the production of hollow beads of polyethylene of controlled size and morphology that comprises the step of:

a) providing a porous functionalised bead of polystyrene II



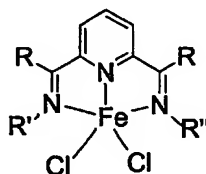
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(II)

wherein A is a flexible arm and is a substituted or unsubstituted alkyl group having from 2 to 18 carbon atoms;

b) dissolving the Iron-based complex of formula I in a solvent;

15



(I)

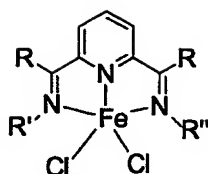
wherein R is the same and is an alkyl having from 1 to 20 carbon atoms and wherein R' and R'' are the same or different and are a substituted or unsubstituted alkyl having from 1 to 20 carbon atoms, or a substituted or substituted aryl having substituents from 1 to 20 carbon atoms;

20

c) saturating the bead of step a) with the solution of step b);
d) evaporating the solvent;

e) retrieving dry beads of the supported catalyst component.

2. The method of claim 1 wherein the R are the same and are alkyl groups having from 1 to 4 carbon atoms.
5
3. The method of any one of the preceding claims wherein R' and R" are the same and are substituted or unsubstituted phenyls.
4. The method of claim 3 wherein the substituents on the phenyls are the same and are isopropyls in positions 2 and 6.
10
5. The method of claim 3 wherein the substituents on the phenyls are the same and are methyls in positions 2, 4 and 6.
6. A supported catalyst component obtainable by the method of any one of claims 1 to 5.
15
7. A supported catalyst system that comprises the supported catalyst component of claim 6 and an activating agent.
20
8. A method for preparing the hollow beads of polyethylene that comprises the steps of:
25
 - a) providing a supported catalyst component wherein the support is a porous functionalised bead of polystyrene and wherein the catalyst component is impregnated on the support and is an iron-based complex of the general formula I



(I)

- 5 b) activating the supported catalyst component with a suitable activating agent;
- c) feeding the ethylene monomer;
- d) maintaining under polymerisation conditions;
- e) retrieving hollow beads of polyethylene of controlled shape and size.

10

9. Hollow beads of polyethylene of controlled size and morphology obtainable by the method of claim 8.

15

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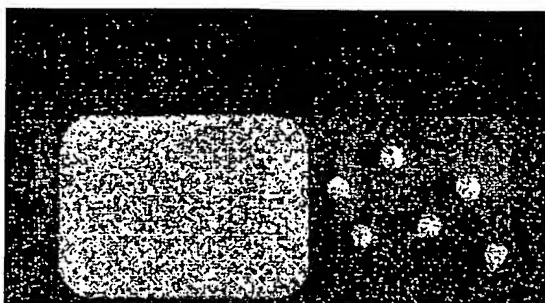


FIGURE 1

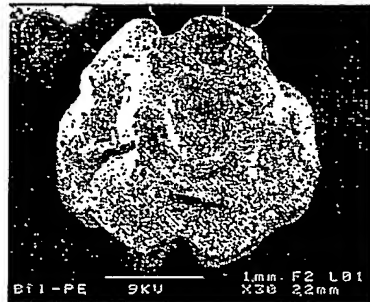


FIGURE 2a

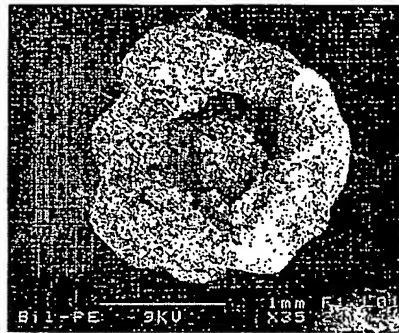


FIGURE 2b

INTERNATIONAL SEARCH REPORT

International Application No
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 066 394 A (METALLGESELLSCHAFT AG) 6 August 1971 (1971-08-06) page 1, line 25 - page 2, line 3 page 4, line 5 - line 30 claims 10,11; examples 1,2,6 -----	9
Y	ROSCOE S B ET AL: "Polyolefin Spheres from Metallocenes Supported on Noninteracting Polystyrene" SCIENCE, AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,, US, vol. 280, 10 April 1998 (1998-04-10), pages 270-273, XP002253630 ISSN: 0036-8075 cited in the application the whole document ----- -/-	1-8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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02/08/2004

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INTERNATIONAL SEARCH REPORT

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PCT/EP2004/050484

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 955 555 A (BENNETT ALISON MARGARET ANNE) 21 September 1999 (1999-09-21) column 8, line 1 - column 12, line 51; examples 43-46 -----	1-8
Y	US 6 489 497 B1 (BROOKHART III MAURICE S ET AL) 3 December 2002 (2002-12-03) column 1, line 41 - column 2, line 40 column 14, line 58 - column 15, line 9; examples 1-23 -----	1-7
Y	SMALL B L ET AL: "IRON-BASED CATALYSTS WITH EXCEPTIONALLY HIGH ACTIVITIES AND SELECTIVITIES FOR OLIGOMERIZATION OF ETHYLENE TO LINEAR ALPHA-OLEFINS" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 120, 1998, pages 7143-7144, XP002934373 ISSN: 0002-7863 cited in the application the whole document -----	1-7

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050484

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2066394	A	06-08-1971	DE 1953399 A1	06-05-1971
			BE 757985 A1	01-04-1971
			FR 2066394 A5	06-08-1971
US 5955555	A	21-09-1999	US 6214761 B1	10-04-2001
			US 6432862 B1	13-08-2002
			US 2002013431 A1	31-01-2002
			US 2001000519 A1	26-04-2001
			AT 213748 T	15-03-2002
			AU 735653 B2	12-07-2001
			AU 5711098 A	15-07-1998
			BR 9714219 A	18-04-2000
			CA 2270243 A1	25-06-1998
			DE 69710776 D1	04-04-2002
			DE 69710776 T2	12-09-2002
			EA 2981 B1	26-12-2002
			EP 1127897 A2	29-08-2001
			EP 0946609 A1	06-10-1999
			HU 0000031 A2	28-05-2000
			ID 21656 A	08-07-1999
			JP 3296496 B2	02-07-2002
			JP 2000516295 T	05-12-2000
			JP 2002302510 A	18-10-2002
			KR 2000057604 A	25-09-2000
			NO 992930 A	10-08-1999
			PL 334300 A1	14-02-2000
			TR 9901352 T2	21-10-1999
			WO 9827124 A1	25-06-1998
US 6489497	B1	03-12-2002	US 6103946 A	15-08-2000
			US 2003036615 A1	20-02-2003
			US 2003050494 A1	13-03-2003
			AT 231830 T	15-02-2003
			AU 748033 B2	30-05-2002
			AU 8569098 A	08-02-1999
			BR 9810587 A	05-09-2000
			CA 2296446 A1	21-01-1999
			CN 1110467 B	04-06-2003
			DE 69811077 D1	06-03-2003
			DE 69811077 T2	06-11-2003
			EP 0994831 A1	26-04-2000
			HU 0003363 A2	28-02-2001
			ID 24095 A	06-07-2000
			JP 2002515917 T	28-05-2002
			NO 20000120 A	10-01-2000
			PL 338145 A1	25-09-2000
			TR 200000004 T2	22-05-2000
			WO 9902472 A1	21-01-1999
			US 2003070188 A1	10-04-2003